MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A
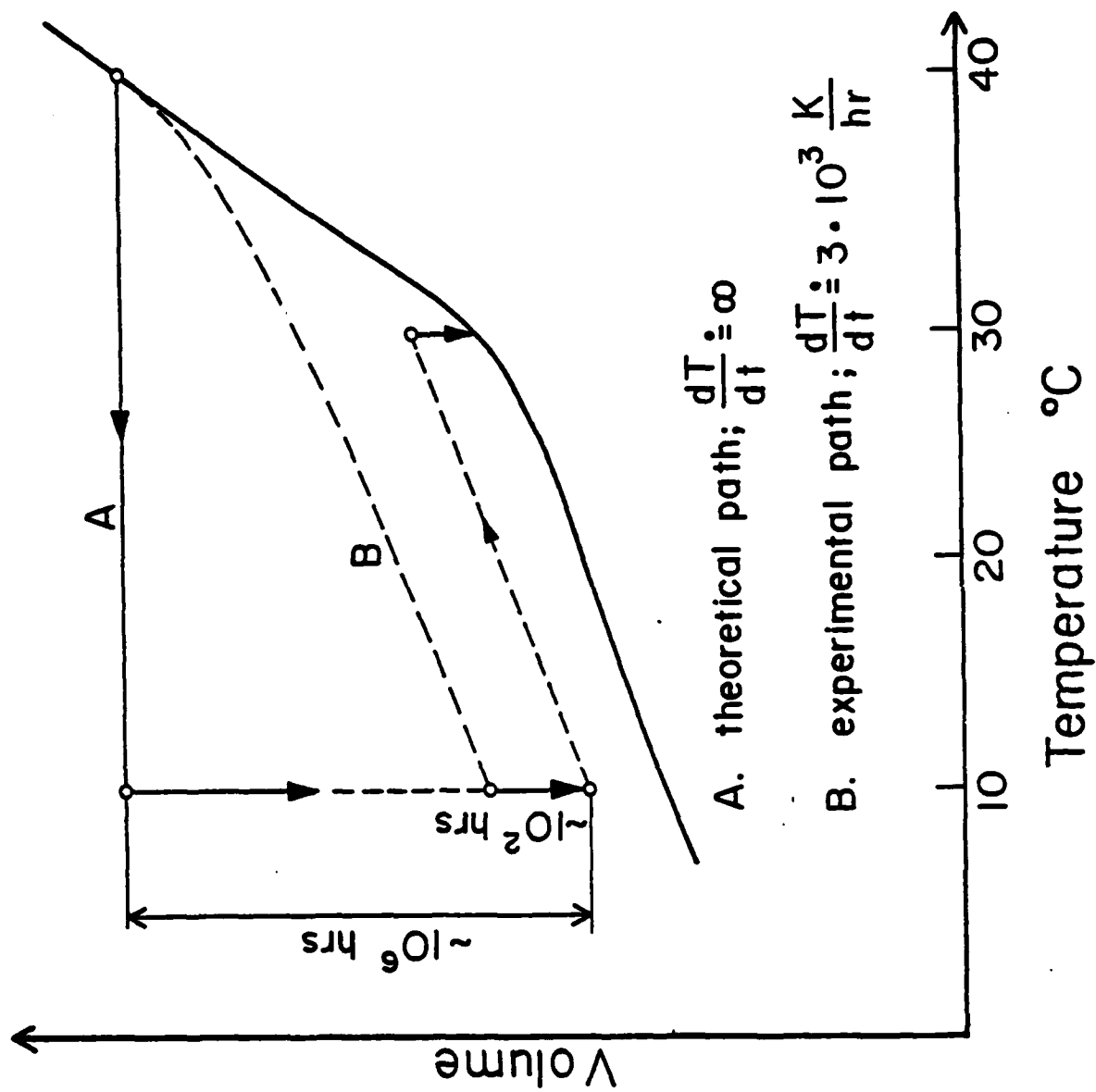
Figure 12.

Volume

Temperature °C

A. theoretical path; $\frac{dT}{dt} \doteq \infty$

B. experimental path; $\frac{dT}{dt} \doteq 3 \cdot 10^3 \frac{K}{hr}$

A

B

~10^2 hrs

~10^6 hrs

PRESSURE INDUCED AGEING OF POLYMERS

I. Emri
Department of Mechanical Engineering
University of Ljubljana, Yugoslavia

W.G. Knauss
Graduate Aeronautical Laboratories
California Institute of Technology
Pasadena, U.S.A.

1. INTRODUCTION

It is a well known fact that polymers change their physical response characteristics in a very significant manner when they are cooled or heated, and especially so when the temperature change spans the glass transition range. This behavior is exemplified, perhaps, most clearly in terms of mechanical relaxation or creep phenomena, though it is equally evident in optical, electrical and masstransport characteristics. These macroscopically observable phenomena are manifestations of the motion of segments of molecule chains relative to each other. This motion is controlled by both the thermal activation of the molecule segments and by the space available to these segments to move. This space is often associated with the concept of "free volume" and has a highly non-linear effect on the segment mobility in the sense that a change has a roughly exponential effect on the rate of segment motion. Thus small changes in free volume will produce very large changes in the mobility of molecule segments, and thus in the physical characterstics of the material.

The change in free volume has been most often connected with thermal changes where it has been associated with time-temperature trade-off in material characterization. However, volume changes arise not only from temperature alterations but also from the absorption of solvents and from mechanical stresses. The latter effect has been studied mostly in the context of the influence of pressure on the glass transition temperature.

Volume changes in polymers can occur over considerably long time scales, and it is a characteristic of these materials that the approach to equilibrium conditions occurs under ever decreasing rates of change. Thus equilibrium behavior of polymers is often only approached but not reached, in particular at temperatures below the glass transition range. Thus Struik [1][1] has observed that creep (or relaxation) behavior of polymers below the glass transition keeps changing for some time after the material has been quenched to the "rigid" state. This change is first rather rapid after quenching and slows down with time to a steady behavior and occurs at a rate that is consistent with the decreasing free volume as it adjusts slowly to equilibrium conditions. The idea here is, that the quenching process ellicits a delayed volume consolidation which entails a lower and lower rate of molecular mobility.

While there seems to be little question regarding the qualitative correctness of these concepts, there is still considerable discussion with respect to the analytical representation or description of these processes. A particular stumbling block in this context seems to be our lack of understanding or experimental assessment of how the free volume approaches equilibrium conditions. On the one hand one finds that the appropriate experiments demand a very high degree of accuracy in volume measurements over long periods of time under extremely well controlled environmental conditions, while, on the other hand one needs to model and represent this behavior analytically in order to ascertain whether the postulated, physics-based model conforms to the measurements. Neither propositions are accomplished easily.

In this paper we shall be concerned with the mechanical behavior of polymers which undergo densification (vitrification) while simultaneously subjected to mechanical straining. In view of several unresolved issues with respect to representing the time-dependent effects of the quenching process we confine ourselves for now to vitrification resulting from the imposition of pressure. The work is almost exclusively computational in nature, based on the experimentally determined uniaxial relaxation behavior which corresponds to that of Solithane 113 (50/50 composition [2]). a polyurethane elastomer manufactured by the Thiokol Chemical Company in Trenton, N.J. The computations were motivated by high pressure experiments on the same material by K. Pae et alii [3], who appear to have used a somewhat differently formulated or processed version of the same material, which did not allow a point by point comparison. We offer these computations, therefore, as an indication of what the effect of time-dependent volume consolidation is on the subsequent mechanical behavior of the polymer. These results are in qualitative agreement with Pae's experiments.

---

1. Numbers in brackets refer to references at the end of the paper.

2. THE MOLECULAR MECHANICS VIEW

In order to relate the following developments to the proper view of molecular mechanics It is appropriate to give consideration to how the molecular motion Is related to the material properties when linearly viscoelatic behavior Is Involved and when the stress state Induces non-linearly viscoelastic response. We start with the proposition that molecular conformations of the molecule chains and the Interdependent motion of their segments give rise to the macroscopically observed time-dependent behavior. Short-time response derives from near-range Interactions while the long-time behavior Is governed by long-range Interactions with a spectral distribution spanning the whole range of time dependence. As long as the macroscopic deformation gradients (strains) are so small that the molecular topology Is not disturbed greatly, (not rubber-like deformations), one can argue that the molecular Interactions as characterized by the spectral distribution functions of relaxation or creep remain essentially unchanged. Stating this assumption Is an alternate way of saying that molecule segments move according to the local constraints offered by neighboring molecules; their rate of motion Is governed by their mutual proximity but the type of motion such as slippage or rotation are not affected strongly. Thus one expects that the distribution functions appropriate for Infinitesimal deformations, i.e. linear viscoelasticity, apply. Specifically, we assume that this understanding holds for both viscoelastic response In shear and volume deformation.

One must admit that our knowledge of molecular motion under a variety of deformation gradients Is rather limited. Thus It Is sometimes suggested, In particular In connection with thermal changes below the glass transition temperature, that certain types of molecular motions cease to occur the lower the temperature becomes. In terms of a phenomenological description such changes would entail changes In the spectral distribution functions. However, In order to Investigate such potential changes It Is necessary to develop Improved descriptions of constitutive behavior, and It Is Just that purpose we have In mind In this contribution. Thus we feel entitled to assume at this stage of development that the spectral functions remain unchanged and leave the examination of deviations from this assumption to future experimental and analytical scrutiny.

We limit ourselves In this Inital Investigation to materials which are thermorheologically simple. This restriction Is assumed primarily because we do not understand very well the reason for the breakdown of thermorheological simplicity from a molecular point of view, though we surmise that the breakdown results from the mechanical Interaction of domains of multiple phases of different constituents In the case of thermorheologically non-simple materials. In the latter context It would be necessary to apply the considerations outlined below to each

constituent in the (molecular) composite but with the constraint of mechanically compatible interactions imposed.

Some aspects of this work have been presented in an earlier publication [4] where the purely mechanical response as well as the effect of certain thermal histories were considered from a unified point of view besides the pressure-ageing. While we shall deal here only with the latter topic, we shall next discuss the complete set of constitutive equations which apply to the former set of conditions and then specialize them to the problem of pressure-ageing.

3. GENERAL EQUATIONS

In adhering to the assumptions stated towards the end of the previous section we choose the material description to be governed by the functions of linear viscoelasticity, except that the time-temperature shift function of thermorheologically simple solids is a more general function of the time-dependent and thus instantaneous volume change, regardless of whether the volume change is induced thermally, mechanically or by solvent swelling. This shift function ϕ is considered to be a functional of the temperature T, of the solvent concentration c and of the mechanically induced dilatation θ, that is

$$\phi = \phi\{T,c,\theta\} \tag{1}$$

where curly brackets denote that ϕ is a functional of T,c, and θ. Doolittle [5] expressed this factor through the free volume by

$$\log\phi = \frac{b}{2.3}(\frac{1}{f} - \frac{1}{f_o}) \tag{2}$$

where f is the fractional free volume defined in terms of the total volume V of the solid and the free volume V_f as

$$f = \frac{V_f}{V} \tag{3}$$

and f_o denotes the fractional free volume at some reference temperature. We consider the free volume to depend on the temperature history and on the strain history, as well as on the history of swelling. We assume that at any instant in time the variable f is a linear functional of the temperature, solvent and of the dilatational stress component.

Linearly viscoelastic volume behavior requires that the dilatation θ is related to the first stress invariant τ_{kk} through

$$\theta(t) = \frac{1}{3} M(t) * d\tau_{kk} \tag{4}$$

where M(t) represents the bulk creep compliance and the star notation indicates Stieltjes convolution; this statement is true within the context of the present discussion provided the volume change is so small that the creep function M(t) is not affected. Similarly, we define a volume creep function for thermal expansion $\alpha(t)$ such that under a sufficiently small thermal excursion history (small volume change) the volume change is given by [4].

$$\Delta V_T = V_o.\alpha(t) * dT \tag{5}$$

where V_o is a Reference volume. Let us leave the question as to whether the time scale of $\alpha(t)$ needs to be "temperature-reduced" moot for the moment. Finally, we would postulate a solvent related volume creep function $\gamma(t)$ which by analogy with (4) and (5) yields volume changes under a hypothetical instantaneous change in concentration "c" to

$$\Delta V_c = V_o.\gamma(t) * dc \tag{6}$$

With the definitions (4),(5), and (6) in mind and the assumption of a linear dependence of the space for molecular motion on the volume change we write the contribution to this motion space f as

$$f = f_o + A \alpha(t)*dT + B M(t)*d\tau_{kk} + C\gamma(t)*dc \tag{7}$$

where the constants A,B, and C need to be generally determined experimentally. They may possibly all have the same value.

Substitution of (7) into the Doolittle equation (2) renders for the instantaneous shift factor

$$\log\phi = \frac{b}{2.3 f_o} \frac{A \alpha(t)*dT + B M(t)*d\tau_{kk} + C \gamma(t)*dc}{f_o + A \alpha(t)*dT + B M(t)*d\tau_{kk} + C \gamma(t)*dc} \tag{8}$$

Note that if $\alpha = const$ and $\tau_{kk} = 0, C = 0$ this expression reduces to the standard Doolittle equation and thus to the WLF equation. In the present case this shift factor is a function of the volume history through the functionals of dilatation, temperature and solvent concentration. More specifically these latter functionals involve also the history of $\phi\{t\}$; for example, $\alpha*dT$ depends on the history of $\phi\{t\}$. Equation (8) is thus an implicit relation for ϕ.

The shift factor modifies the (material-internal) rate with which viscoelastic functions change. If an environmental change causes a constant

change in the volume components, then ϕ multiplies the relaxation or retardation time in the material functions. We now assert that in general the argument in the creep functions $\alpha(t)$, $\gamma(t)$ and M(t) must be "reduced" by the instantaneous shift factor, where the shift function ϕ is itself a function of the environmental histories.

Lee suggested that the "standard" time-temperature shifting, demonstrated for time-independent temperatures, be valid instantaneously under transient thermal conditions [6,7]. We shall assume similarly that the shift relation (8) for ϕ is valid instantaneously while incorporating the effect of mechanically and solvent induced volume change. We have thus for a reduced time for the material behavior

$$dt' = \frac{dt}{\phi\{t\}} \quad or \quad t'(t) = \int_0^t \frac{du}{\phi\{T(u),c(u),\theta(u)\}} \tag{9}$$

Let τ_{ij} and ϵ_{ij} denote, respectively, the components of the Cauchy stress and of the (small) strain. In terms of the deviatoric stresses S_{ij} and deviatoric strains e_{ij} the stress-strain relations are (the summation convention for repeated indices applies)

$$S_{ij} = 2 \int_{-\infty}^t \mu[t'(t) - \xi'(\xi)]\frac{\partial e_{ij}(\xi)}{\partial \xi} \, d\xi \tag{10a}$$

$$\tau_{kk} = 3 \int_{-\infty}^t K[t'(t) - \xi'(\xi)]\frac{\partial \theta(\xi)}{\partial \xi} \, d\xi, \quad K*M = t \tag{10b}$$

$$t'(t) - \xi'(\xi) = \int_\xi^t \frac{du}{\phi\{T(u),c(u),\theta(u)\}} \tag{9a}$$

along with (8) for $\phi\{t\}^2$

Equations (8), (9), and (10) are coupled and implicit relations for the stress history if, e.g., the strain history is prescribed at a material point[3] in dependence on the presumably known thermal and solvent history. Alternately, if the stress and environmental histories are prescribed - in particular when the stress is zero - these equations are implicit relations for the time-dependent volume change ϵ_{kk}.

---

2. Note that with the present notation ϵ_{kk} $(t) = \theta(t) + \alpha(t)*dT + \gamma(t)*dc$.

3. We choose not to address here the wider problem of thermal and solvent *diffusion* and their interaction with the state of stress or its field.

4. EFFECT OF PRESSURE HISTORY ON UNIAXIAL DEFORMATION BEHAVIOR

In this section we are interested in demonstrating the profound effect which the simple concept of time-dependent volume change has on viscoelastic behavior when such volume change is allowed to affect the time-shift phenomenon. Struik's experiments revealed a time-dependent drift of properties toward an equilibrium behavior after initial quenching. Because no chemical changes were involved this change process was termed "physical ageing." Similar to the experiments on physical ageing by Struik [1] time dependent volume compaction under pressure changes the viscoelastic response of the material, tending to "push" the solid "towards glassy behavior" and we may then speak of an ageing process induced by pressurization. On the other hand, the imposition of a tensile stress causes an opposing trend. Let us consider uniaxial deformation histories with constant rate of straining and consider the response under two types of pressure histories: In one case let the pressure be applied just prior to or with the start of uniaxial straining; in the other case let straining start at various times after the pressure has been imposed. In this latter case the effect of time dependent volume consolidation (ageing) on the time scale of non-linearly viscoelastic will become apparent. Let us turn first to the case of

a) Simultaneous Pressurization and Straining.

We assume the temperature to remain constant[+] throughout these strain histories and consider a sudden step pressure P applied at time t=0 while a constant strain rate history $\dot{\epsilon}_o = const$ is imposed simultaneously. Thus,

$$\tau_{kk} = 3.P.h(t) \tag{11}$$

and

$$\epsilon_{11} = \dot{\epsilon}_o.t, \quad t \geq 0 \tag{12}$$

Let E(t) be the relaxation modulus for (infinitesimal) uniaxial deformation as shown in Figure 1 and represented by a Dirichlet series

$$E(t) = E_o + \sum_{n=1}^{18} E_n e^{-t/\tau_n} \tag{13}$$

where the E_n and τ_n are given in Table I. These coefficients were determined in a collocation procedure based on the data in Figure 1. Further,

---

4. Actually pressurization produces in general also a temperature rise, which we neglect in these illustrations.

Table I.
$$E_o = 26.613 \text{ [bar]}$$

n	E_n [bar]	τ_n [min]	
1	677.827	1	10^{-8}
2	8.527	3.162	10^{-8}
3	545.344	1	10^{-7}
4	876.463	3.162	10^{-7}
5	564.947	1	10^{-6}
6	584.252	3.162	10^{-6}
7	340.672	1	10^{-5}
8	286.495	3.162	10^{-5}
9	262.926	1	10^{-4}
10	120.850	3.162	10^{-4}
11	22.663	1	10^{-3}
12	28.793	3.162	10^{-3}
13	5.446	1	10^{-2}
14	3.076	3.162	10^{-2}
15	1.561	1	10^{-1}
16	0.253	3.162	10^{-1}
17	0	1	
18	0.072	3.1622	

let M be the corresponding bulk creep compliance similarly represented by

$$M(t) = M_o + \sum_{n=1}^{9} M_n(1 - e^{-t/\chi_n}) \tag{14}$$

which is also indicated in Figure 1, the coefficients M_n and χ_n being listed in Table II. In view of the fact that we are concerned in this section with qualitative results we estimated the coefficients M_i from data offered by Pae [3] through collocation.

Table II.
$$M_o = 9.1811 \ 10^{-5} \ [bar^{-1}]$$

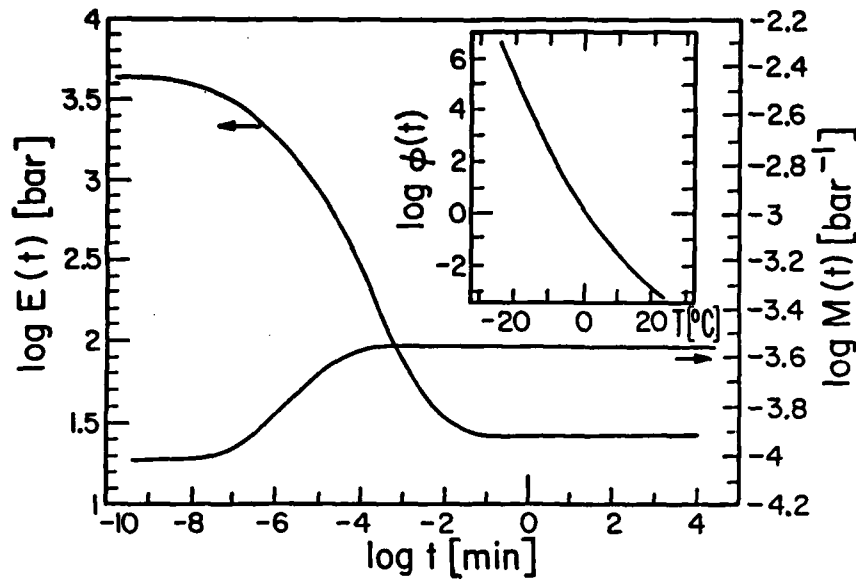| n	M_n [bar^{-1}]	χ_n [min]	
1	5.619 10^{-7}	3.162	10^{-8}
2	17.826 10^{-8}	1	10^{-7}
3	0.294 10^{-4}	3.162	10^{-7}
4	0.192 10^{-4}	1	10^{-6}
5	0.415 10^{-4}	3.162	10^{-6}
6	0.343 10^{-4}	1	10^{-5}
7	0.401 10^{-4}	3.162	10^{-5}
8	8.468 10^{-6}	1	10^{-4}
9	10.351 10^{-6}	3.162	10^{-4}

Figure 1. Relaxation modulus for uniaxial state of stress. Bulk creep compliance and thermal shift factor used for pressure related computations on Solithane 113 (50/50).

If τ_{11} and ϵ_{11} are the increments of stress and strain from the pressure and the volume strain the stress strain relations are then

$$\tau_{11}(t) = \int_0^t E[t'(t) - \xi'(\xi)]\,\frac{d\epsilon_{11}(\xi)}{d\xi}$$

$$= \dot{\epsilon}_o \int_0^t E[t'(t) - \xi'(\xi)]\,d\xi \tag{15a}$$

$$\theta(t) = \int_0^t M[t'(t) - \xi'(\xi)]\,\frac{d}{d\xi}\,[P(\xi) + \frac{1}{3}\,\tau_{11}(\xi)]\,d\xi \tag{15b}$$

where, again

$$t'(t) = \int_0^t \frac{du}{\phi\{T,O,\theta(u)\}} \quad \text{and} \quad \xi'(\xi) = \int_0^\xi \frac{du}{\phi\{T,O,\theta(u)\}} \tag{16}$$

$$\ln\phi\{T,O,\theta\} = -\frac{b(T)}{f_o(T)}\,\frac{B.\theta(t)}{f_o(T)+B.\theta(t)} \tag{17}$$

In these computations we used B=1 because we do not know K(t) or M(t) closely. The properties in Figure 1 are defined for $0°C$. To make use of these at different temperatures we shift the functions according to the

shift factor inset in that figure. However, the parameters b(T) and $f_o(T)$ in (17) must be adjusted to the appropriate temperature [8]. It remains to evaluate equations 15-17 numerically.

In Figure 2 we show for Reference purposes the non-linear response at -20^oC, 2^oC below the glass transition, under zero imposed pressure as the uniaxial strain rate is varied. One notices the appearance of a yield phenomenon, with the yield stress and yield strain increasing with the strain rate.
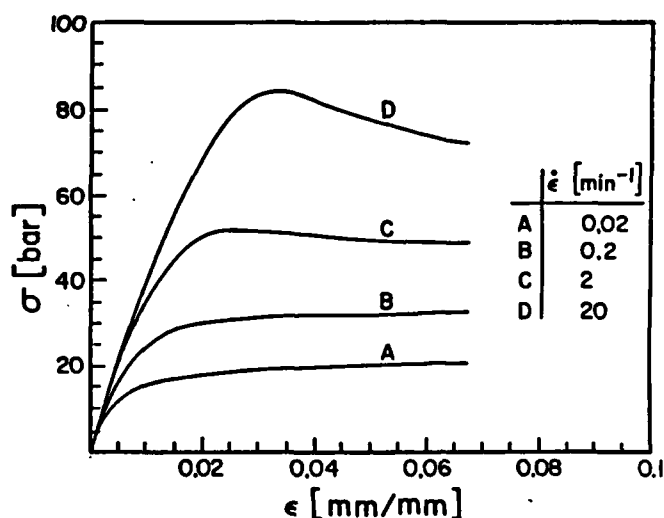

Figure 2.   Uniaxial Stress response to constant strain rates for atmospheric pressure and for properties shown in Figure 1.

In terms of the present physical model the appearance of the yield phenomenon has the following explanation. The imposition of a pressure causes a decrease in the (free) volume and thus a vitrification of the solid. However, the imposition of a tensile stress counteracts this vitrification process and produces, with increasing strain (stress) an increase in the rate of molecular relaxation through a change in the time-shift function. Whether one achieves a yield phenomenon or not depends on the competition between the pressure-induced solidification and the tension-induced volume increase. Once the two rates roughly balance each other the stress reaches a plateau such as seems to be approximately the case for curve "B" in Figure 2 . For higher strain rates the tension-induced volume increase occurs faster than the solidification due to the imposition of the pressure thus leading to a relaxation process which overpowers the stress increase due to straining. We shall see that this phenomenon occurs again later in an even more pronounced fashion depending on the past vitrification history of the material.

Figure 3a illustrates the effect of increasing the pressure while keeping the temperature constant just below the glass transition ($-20°C$) and for a fixed strain rate of $\dot\epsilon=20\text{min}^{-1}$. Note again the occurance of the yield phenomenon, with the yield stress increasing with pressure. This observation merely substantiates the fact that a higher environmental pressure requires a higher tension in order to overcome the pressure-induced vitrification process. However, the yield phenomenon appears to depend also on the fact that the volume change induced by the uniaxial straining lags behind the strain due to the viscoelastic volume response. This statement becomes evident when one looks at the identical strain and pressure histories but at a temperature well above the glass transition temperature. Thus, Figure 3b shows results for the same pressure and strain histories as Figure 3a, but about 12 degrees above the glass temperature. Here one notes the absence of the yield behavior because first, the temperature is so high that pressure-induced volume decrease occurs almost instantaneously, and second, the volume change produced by the uniaxial straining is very much in phase with the strain so that any relaxation process occurs simultaneously with the straining rather than being delayed viscoelastically.
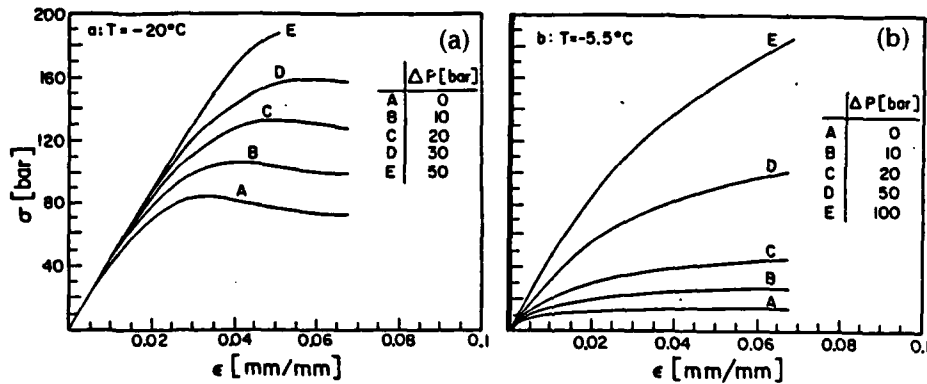

Figure 3.   Simultaneous pressure application and imposition of strain
             rate of $\dot\epsilon=20$ min^{-1}. (a) $T= - 20°C$; (b) $T= - 5.5°C$.

b) Pressure Ageing

Consider next the effect of imposing pressure on the material at time $t=0$ and subjecting it to straining after different times t_1 have passed. The equations governing this history are similar to (14) and are given by

$$\tau_{11}(t) = \dot\epsilon_o h(t - t_1)\int_{t_1}^{t} E[t'(t) - \xi'(\xi)]d\xi \tag{18a}$$

$$\theta(t) = P.M[t'(t)] + h(t - t_1)\frac{1}{3} \int_{t_1}^{t} M[t'(t) - \xi'(\xi)]\frac{d\tau_{11}(\xi)}{d\xi} d\xi \tag{18b}$$

where $t'(t)$ and $\zeta'(t)$ are still given by (16) and (17).

Solutions to these equations for several situations are given in Figures 4a to 4d. Several features stand out and deserve attention: The effect of the time dependent consolidation process is clearly evident in that longer times between pressurization and straining gives rise to markedly stiffer material response and an increase in yield stress with this ageing time as noted in reference 3. Again, the competitive effect of pressure-induced consolidation with the tension-induced volume increase is very evident as in the cases considered in Figures 3a and b, except that the effect is more pronounced because with increased ageing time the consolidation can progress more completely and thus give rise to more pronounced relaxation upon reaching a sufficiently high tension-

(a) $\dot{\varepsilon}=0.002$ min^{-1}, $T=-20°C$
(2°C below Tg)

(b) $\dot{\varepsilon}=0.02$ min^{-1}, $T=-20°C$

(c) $\dot{\varepsilon}=20$ min^{-1}, $T=-20°C$
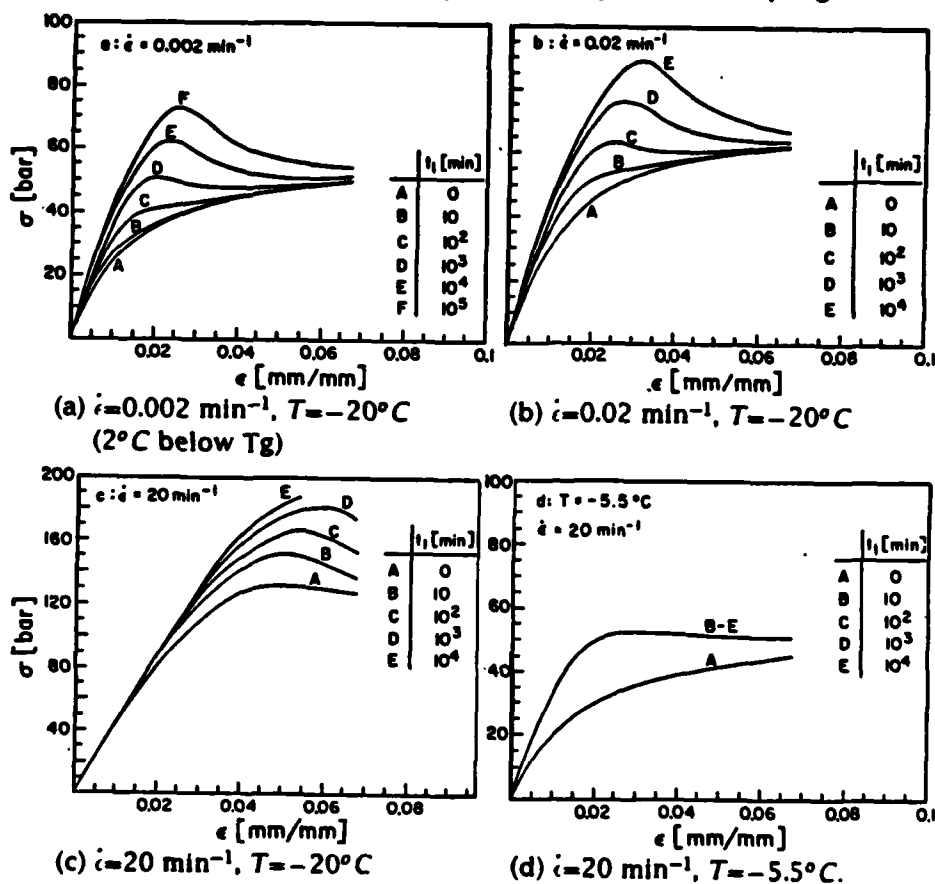
(d) $\dot{\varepsilon}=20$ min^{-1}, $T=-5.5°C$.

Figure 4. Uniaxial stress-strain behavior superposed on pressure of $\Delta p = 20$ bar.

Induced dilatation. Finally, Figure 4c illustrates again the behavior at about 12 degrees above the glass transition; one notes again that at this elevated temperature the adjustment of the (free) volume to equilibrium conditions occurs very rapidly so that the tension-induced volume change is very much in phase with the strain. As a consequence the time-dependence of the bulk deformation barely enters the considera-

tions and the stress-strain curves for the material "aged" to varying degrees are virtually indistinguishable. Clearly, Figures 4a-c illustrate the importance of the time-dependent volume behavior of polymers in their non-linear mechanical characteristics.

5. CONCLUDING REMARKS

We have illustrated, on hand of sample calculations, the importance of time-dependent volume consolidation on the mechanical, non-linearly viscoelastic response of polymers. The temperature and deformation rates play an important part in this behavior, in large measure because these variables determine the rate of change of the (free) volume.

We point out in closing this presentation that the non-linear effects considerered here derive only from the single physical phenomenon of molecular motion and do not incorporate such macroscopic physical phenomena as crazing or fracturing, both of which effects give rise to (additional) non-linear "consitutive" behavior. The presently discussed behavior is, however, a precursor to the latter physical phenomena and can hardly be neglected in their time-dependent description. Thus one would expect that the "molecular" yielding exemplified here is the reason why zones of mechanically unstable material behavior develop in materials around zones of stress concentration, which zones develop possibly into craze zones.

6. REFERENCES

1. Struik, L.C.E., - *Physical Ageing in Amorphous Polymers and Other Materials,* Elsevier Sci. Pub. Co., Amsterdam, 1978.

2. Muller. H.K., Knauss, W.G., - The Mechanical Characterization of Solithane 113 in the Swollen and Unswollen State, GALCIT SM Report 67-8, CHECIT PL 68-2, California Institute of Technology, Pasadena, California, U.S.A.

3. Pae, K.D., Kijayan, K., Tang, C.L., - Ageing Time Dependence of Mechanical Properties of Elastomeric Glasses at High Pressure. Personal communication in the form of an undated report draft.

4. Knauss, W.G., Emri, I. - Volume Change and the Non-Linearly Thermo-Viscoelastic Constitution of Polymers, GALCIT SM Report 85-26; to appear in Polymer Engineering and Science, edited by A. Yee, 1987.

5. Doolittle, A.K., - Studies in Newtonian Flow. II. The Dependence of the Viscosity of Liquids on Free-Space, J. Appl. Phys., *22,* 12, p. 1471, 1951.

END

12-86

DTIC